

## CONSTRAINING OXYGEN AND SULFUR FUGACITY IN VENUS WEATHERING EXPERIMENTS IN THE GLENN EXTREME ENVIRONMENT RIG. A. R. Santos<sup>1</sup>, M. S. Gilmore<sup>1</sup>, M. Yu. Zolotov<sup>2</sup>, and V. Tu<sup>3</sup>

<sup>1</sup>Department of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459 (asantos@wesleyan.edu), <sup>2</sup>School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, <sup>3</sup>Jacobs JETS II, Houston, TX 77058.

**Introduction:** Experimental efforts to understand chemical weathering of Venus surface rocks and minerals have been undertaken using a range of methods and conditions [e.g., 1-4]. A challenge with many of these experiments is measuring and maintaining the gas composition at the desired values because of the lack of instruments and sensors that can monitor gas compositions within vessels at Venus conditions. Thus, the oxygen fugacity,  $f_{O_2}$ , and sulfur fugacity,  $f_{S_2}$ , for Venus experiments are often not well known or constrained. Oxygen and sulfur fugacities dictate the stability of many minerals such as iron oxides and sulfides, and thus play a crucial role in weathering reactions [e.g., 5].

The  $f_{O_2}$  and  $f_{S_2}$  at the lowlands of Venus is not well measured, but calculations based on best measurements have estimated these values to be within a range of  $\log f_{O_2} = -20$  to  $-21.7$  [6], and  $\log f_{S_2} \sim -4.6$  to  $-5.7$  at the conditions of the modal radius (467 °C, 95.6 bars) [5]. Due to the limited data from Venus and different methodologies for determining mineral stability, it is debated which iron sulfides (e.g., pyrite ( $FeS_2$ ) vs. pyrrhotite ( $Fe_{(1-x)}S$ )) or oxides (magnetite ( $Fe_3O_4$ ) vs. hematite ( $Fe_2O_3$ )) are the stable phases in the lowlands, though most models suggest pyrrhotite is not stable [5]. The calculated value of  $f_{O_2}$  for the near surface atmosphere is within error of the magnetite-hematite buffer, making it difficult to determine which of these phases would be stable [5,6]. Iron in minerals is predicted to be one of the most prominent reactants with atmospheric gases in chemical equilibrium models, and it is important to know  $f_{O_2}$  and  $f_{S_2}$  in experiments aimed at understanding gas-solid type interactions on Venus.

The Glenn Extreme Environment Rig (GEER), located at NASA Glenn Research Center (GRC), is able to simulate complex Venus surface conditions. It is capable of reproducing the surface temperature and pressure of Venus for long durations (months), with mixtures of up to 9 gases that can be adjusted and monitored during the course of an experiment using a gas mixing and injection system [4,7]. The facility is equipped with an in line gas chromatograph (GC) to measure selected gas species in extracted gas aliquots [4,7]. Two recent studies using this facility, those of Radoman-Shaw et al. [4] and Santos et al. [7], appear to have conflicting results regarding the stability of Fe oxides and sulfides. Radoman-Shaw et al. [4] report reaction of pyrite to produce Fe oxide, and reaction of an Fe-Ti oxide to produce

secondary Fe oxide, while Santos et al. [7] report stability of pyrite and reaction of an Fe-Ti oxide to form a secondary Fe sulfide. This suggests the  $f_{O_2}$  and/or  $f_{S_2}$  within these experiments may have been different, despite employing similar  $T$ - $P$  conditions and the same starting gas composition. Neither experiment could include *in situ* sensors to monitor the critical variables of  $f_{O_2}$  and  $f_{S_2}$ .

In light of these conflicting results, we have used the GEER facility to conduct a 60-day weathering experiment that included a suite of samples for the express purpose of constraining the  $f_{O_2}$  and  $f_{S_2}$  of the experiment. This method relies on identifying reaction products in a series of solid samples that can be compared to phase equilibrium conditions and phase diagrams calculated for the experimental conditions. This method will provide information on the average conditions within the experimental chamber, and is supported by continuous observations using the DAVINCI V/Ox sensor prototype [8]. This method is subject to the kinetics of gas-solid type reactions, meaning secondary mineral layers may not reflect every change in experiment conditions because the timescale of the change could be faster than the reaction rate. Despite these caveats, using this dedicated sample suite would allow us to better bracket the conditions within the vessel than was possible in prior experiments.

**Methods:** The samples used to bracket fugacity are shown in Table 1. Samples include both natural minerals (prepared as chips and powders), reagent grade oxide and sulfide powders, and reagent grade metal powders and plates.

At the GEER facility, samples were placed in high walled alumina crucibles (powders) and trays (chips). This experiment was designed to simulate the lowlands surface environment of Venus (460°C, 93 bars) using the atmospheric composition listed in Table 2. The temperature and total pressure in the vessel were monitored by thermocouples and pressure transducers inside the vessel, while concentrations of  $CO_2$ ,  $N_2$ ,  $SO_2$ ,  $CO$ ,  $COS$ , and  $H_2S$  were monitored through GC analysis of extracted gas aliquots. Gas composition corrections were made (via addition) as needed in order to keep concentrations within specified ranges. The experimental run products were stored in a desiccator.

Table 1: Samples used to constrain  $f_{O_2}$  and  $f_{S_2}$  in the GEER experiment. Buffer mineral mixtures include iron-quartz (IQ), magnetite-hematite (MH), and quartz-fayalite-magnetite (QFM). Italics-powder and chip sample, <sup>r</sup>-reagent, \*-sample only present as chip, non-italics-sample only present as powder.

Category	Sample	Category	Sample
Metals	Fe metal	Oxides	<i>Ilmenite</i>
	Re foil*		<i>Chromite</i>
	Cobalt metal*		<i>Hematite</i>
Sulfides	<i>Pyrite</i>		<i>Magnetite<sup>r</sup></i>
	<i>Pyrite<sup>r</sup></i>		<i>Hematite<sup>r</sup></i>
	<i>Chalcopyrite</i>		<i>Magnetite</i>
	<i>Pyrrhotite</i>	Buffer Mixtures	IQ
	<i>Troilite<sup>r</sup></i>		MH
Silicates	<i>Fayalite</i>		QFM
	<i>Olivine</i>		

Table 2: Gas composition of the experiment. Initial composition based on reported values for Venus based on [9].

Species	Specified Initial Composition	Measured range
CO <sub>2</sub>	96.5±0.8%	95.5-97.6 %
N <sub>2</sub>	3.5±0.8%	3.1-3.8%
SO <sub>2</sub>	150±30 ppmv	6.5-180 ppm
CO	17±1.4 ppmv	2.1-49.2 ppm
COS	4.4±1 ppmv	4.4-41.5 ppm
H <sub>2</sub> S	3±2 ppmv	1.0-4.8 ppm
H <sub>2</sub> O	30 ppmv	N/A
HCl	0.4 ppmv	N/A
HF	5 ppbv	N/A

**Preliminary Results:** The experiment was run for 60 days of Venus conditions in the summer of 2022 (see [10]). GC measurements show the SO<sub>2</sub> content in the experiment atmosphere decreased at an average rate of 2.7 ppm/hr over the course of the experiment. This required frequent gas corrections, and represents a deviation in experiment behavior from what was seen in [4] and [7], although those experiments did not include mineral powders, which will have a higher surface area.

**Sample analysis.** Visual examination of samples suggests some have reacted on the experimental time-scale. Samples of pyrrhotite went from having a golden, metallic luster to having what appears to be a dull, patchy coating (Fig. 1A). Cobalt metal underwent a similar transformation, losing a metallic luster to form a rough, dull coating. The powdered iron sample appears to have formed small, scattered blooms of a dull, golden material (Fig. 1B). These data suggest the experiment is outside of the stability field of pyrrhotite, cobalt metal, and Fe metal, but further analysis is needed to determine if the apparent secondary minerals formed are oxides or sulfides.

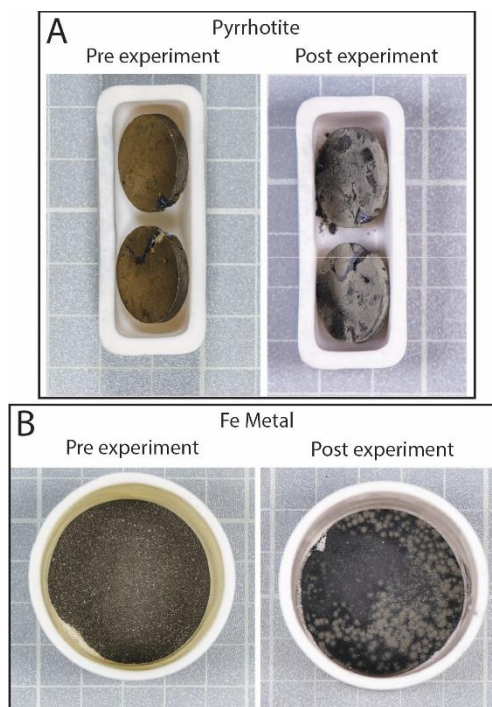


Figure 1: Photographs of pyrrhotite chips (A) and iron metal powder (B) before and after the 60-day GEER experiment. Squares in background are 1 cm.

**Next Steps:** Powdered samples will be analyzed by quantitative powder XRD at NASA Johnson Space Center to identify changes to mineralogy, Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopy (EDS) and Visible-Near Infrared Spectroscopy (VNIR) at Wesleyan University to determine changes to sample surface morphology and mineralogy. Iron-bearing samples will be measured by Mossbauer spectroscopy at Mount Holyoke College to determine Fe oxidation state. Chip samples will be analyzed by VNIR and SEM/EDS, allowing determination of surface morphology and composition. Interpretation of results will be aided by calculations of chemical equilibria of individual gas-solid type reactions and in selected multicomponent gas-solid systems.

**Acknowledgments:** This work is funded by a NASA SSW grant 80NSSC19K0549 to MSG. We thank our collaborator D. Dyar who will be providing Mossbauer spectroscopy analyses.

**References:** [1] Cutler K.S. et al. (2020) *PSJ*, 21, 10pp. [2] Berger G. et al. (2019) *Icarus*, 329, 8-23. [3] Teffeteller H. et al. (2022) *Icarus*, 384, 115085. [4] Radoman-Shaw B.G. et al. (2022) *MAPS*, 57, 1796-1819. [5] Zolotov M.Yu. (2018) *RIMG* 84, 351-392. [6] Fegley et al. (1997) *Icarus*, 125, 416-439. [7] Santos A.R. et al. (2023) *JGR: Planets*, in press. [8] Izenberg N. et al. (this meeting). [9] Lodders K. and Fegley B. (1998) *The Planetary Scientist's Companion*. Oxford University Press. [10] Gilmore M.S. and Santos A.R. (this meeting).